

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 199 138
A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 86104308.1

(51) Int. Cl.4: C07C 43/17, C08F 214/18

(22) Date of filing: 27.03.86

(30) Priority: 28.03.85 JP 65185/85
28.03.85 JP 65186/85

(43) Date of publication of application:
29.10.86 Bulletin 86/44

(84) Designated Contracting States:
DE FR GB IT

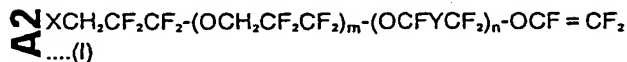
(71) Applicant: DAIKIN INDUSTRIES, LIMITED
No. 1-12-39, Umeda Kita-ku
Osaka-shi Osaka-fu(JP)

(72) Inventor: Oka, Masahiko
18-6, Hiyoshi-dai 2-chome
Ohtsu-shi Shiga-ken(JP)
Inventor: Yutani, Yuji
2-1, Kozu Minami-ku
Osaka-shi Osaka-fu(JP)
Inventor: Tomoda, Masayasu
2-24-7, Nango
Ohtsu-shi Shiga-ken(JP)
Inventor: Kishine, Mitsuru
6-26, Matsuyama-cho
Ohtsu-shi Shiga-ken(JP)
Inventor: Shimizu, Tetsuo
27-104, Shinkoriyama 2-chome
Ibaraki-shi Osaka-fu(JP)

(74) Representative: Lehn, Werner, Dipl.-Ing. et al
Hoffmann, Eitle & Partner Patentanwälte
Arabellastrasse 4 (Sternhaus)
D-8000 München 81(DE)

(54) Novel fluorovinyl ether and copolymer comprising the same.

(57) A fluorovinyl ether of the formula:



wherein X is a hydrogen atom or a halogen atom -
(e.g. fluorine, chlorine, bromine and iodine); Y is a
fluorine atom or a trifluoromethyl group; m is an
integer of 0 to 5; and n is 0, 1 or 2, which can
modify a polymer of at least one ethylenically un-
saturated compound.

NOVEL FLUOROVINYL ETHER AND COPOLYMER COMPRISING THE SAME

FIELD OF THE INVENTION

The present invention relates to a novel fluorovinyl ether and a copolymer comprising the same. More particularly, it relates to a novel fluorovinyl ether useful as a modifier of a polymer comprising an ethylenically unsaturated compound, and a copolymer comprising at least one ethylenically unsaturated compound and the novel fluorovinyl ether.

BACKGROUND OF THE INVENTION

Copolymerization of a fluoroolefin with other fluoroolefin or non-fluoroolefin provides a copolymer having wide range of properties from a resin to an elastomer depending on the kinds and/or contents of the fluoroolefin and other monomer. Therefore, the copolymer of the fluoroolefin finds various applications, for example, as a part of a machinery such as an O-ring, a flange seal, a gasket, a diaphragm and a liner and is particularly useful in a field in which excellent resistance to heat and/or corrosion is required.

For producing an elastomeric polymer, a cross linking method plays an important role. Since a copolymer of the fluoroolefin is thermally and chemically stable, it is difficult to cross-link it. For cross-linking the copolymer of fluoroolefin, it has been proposed to copolymerize a monomer which provides a cross-linking site to the polymer. As the monomer providing the cross-linking site, there have been proposed an unsaturated compound having a perfluorophenoxy group (cf. Japanese Patent Publication No. 11823/1972), a nitro group - (Japanese Patent Publication 26303/1970 and Japanese Patent Kokai Publication (unexamined) No. 61119/1974) or a bromine atom (Japanese Patent Publication Nos. 4115/1978 and 1585/1979). However, it takes longer time to cross-link the copolymer containing such monomer, and the cross-linked product has still unsatisfactory physical properties.

Among the resinous polymer of the fluoroolefin, polytetrafluoroethylene (hereinafter referred to as "PTFE") is most widely used and molded to form various articles. Conventionally, PTFE having a molecular weight of 1,000,000 or more is used for molding. However, since PTFE having such high molecular weight has large melt viscosity, for example, of 1×10^6 PaS at 380°C , its melt processing is very difficult. To decrease melt viscosity of PTFE, some copolymers of tetrafluoroethylene and other fluorine-containing monomers are proposed

and commercially available. Such copolymers as contain other monomer in an amount not larger than 2 % by mole are called as modified PTFE and processed by substantially the same molding method as PTFE. Examples of the monomer are $\text{CF}_2\text{CF}=\text{CF}_2$, $\text{C}_2\text{F}_5\text{OCF}=\text{CF}_2$, $\text{ClCF}=\text{CF}_2$, $\text{C}_6\text{F}_5\text{CH}=\text{CH}_2$ and mixtures thereof. It is still highly desired to provide a modified PTFE having further improved performances in molding in comparison with pure PTFE.

SUMMARY OF THE INVENTION

One object of the present invention is to provide a novel fluorovinyl ether which can provide a cross-linking site to a polymer of an ethylenically unsaturated compound, particularly a fluorine-containing ethylenically unsaturated compound.

Another object of the present invention is to provide an elastomeric polymer comprising an ethylenically unsaturated compound which can be cross-linked in a shorter period of time.

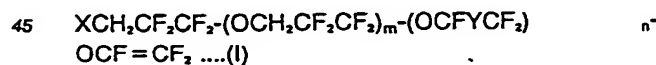
Further object of the present invention is to provide an elastomeric polymer comprising an ethylenically unsaturated compound a cross-linked product of which has good physical properties such as tensile strength, elongation, heat resistance and compression set.

Yet another object of the present invention is to provide an elastomeric polymer having improved low temperature properties.

Yet further object of the present invention is to provide a modified PTFE of a granule form which is molded by compression molding and ram injection molding to provide an article having improved creep resistance after sintering.

Still another object of the present invention is to provide a modified PTFE of a fine powder form which can be molded by paste extrusion to provide an article having considerably improved mechanical strength before sintering.

These and other objects are accomplished by a fluorovinyl ether of the formula:



wherein X is a hydrogen atom or a halogen atom - (e.g. fluorine, chlorine, bromine and iodine); Y is a fluorine atom or a trifluoromethyl group; m is an integer of 0 to 5; and n is 0, 1 or 2, and a copolymer comprising at least one ethylenically unsaturated compound and the fluorovinyl ether (I).

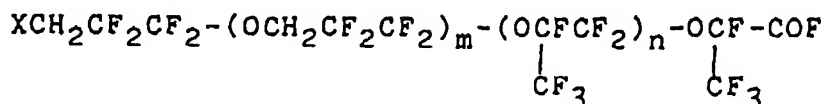
DETAILED DESCRIPTION OF THE INVENTION

The fluorovinyl ether (I) may be derived from a corresponding acyl fluoride which is prepared by a method described in U.S. Patent Application No. 684, 344 and European Patent Application No. 84

116 103.7 (EP-A-0148490) or U.S. Patent Application No. 684,345 and European Patent Application No. 84 116 003.9 (EP-A-0148482), the disclosures of which are hereby incorporated by reference.

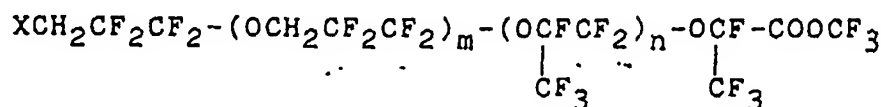
In case where Y in the formula (I) is a trifluoromethyl group, a corresponding acyl fluoride is converted to the fluorovinyl ether as follows:

An acyl fluoride of the formula:



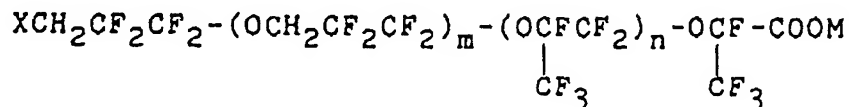
15

is reacted with a lower alcohol such as methanol to form an ester of the formula:



25

The resulting ester is then reacted with an alkali metal hydroxide (MOH) such as sodium hydroxide to form a salt of the formula:



The salt is heated at a temperature of 150 to 250°C in a stream of an inert gas such as nitrogen or under reduced pressure to form the fluorovinyl ether (I).

The ethylenically unsaturated compound which is copolymerized with the fluorovinyl ether (I) may be any one of conventional compounds. Specific examples of the ethylenically unsaturated compound are fluorine-not-containing ethylenically unsaturated compound (e.g. ethylene, propylene, butylene, vinyl carboxylate such as vinyl acetate, vinyl ether such as methyl vinyl ether and ethyl vinyl ether, vinyl chloride, vinylidene chloride, acrylic acid and methacrylic acid), and fluorine-containing ethylenically unsaturated compounds - (e.g. tetrafluoroethylene, trifluoroethylene, chlorotrifluoroethylene, vinyl fluoride, vinylidene fluoride, hexfluoropropylene, pentafluoropropylene, hexafluoroisobutene, perfluorocyclobutene, perfluoro(methylcyclopropylene), perfluoroallene, α,β,β-trifluorostyrene, perfluorostyrene, perfluoroalkyl vinyl ether such as perfluoro(methyl vinyl

ether) and perfluoro(propyl vinyl ether), perfluoro(alkyl vinyl polyether), polyfluoroacrylic acid, polyfluorovinyl acetate, polyfluorovinyl ether sulfonate and polyfluorodienes).

The amount of the fluorovinyl ether (I) in the copolymer depends on the kind of the copolymer to be produced. In general, it is from 0.01 to 60 % by mole based on the total mole of other monomer(s). To provide cross-linking sites to the elastomeric copolymer, the amount of the fluorovinyl ether (I) is from 0.01 to 5 % by mole, preferably from 0.1 to 5 % by mole based on the mole of other monomer(s). To improve the low temperature property of the elastomeric copolymer, it is from 5 to 60 % by mole, preferably from 10 to 50 % by mole based on the mole of other monomer(s). To modify the resinous polymer such as PTFE, it is from 0.01 to 2 % by mole, preferably from 0.03 to 1 % by mole based on the mole of other monomer(s).

According to the first preferred embodiment of the present invention, an elastomeric copolymer comprises 50 to 95 % by mole of repeating units derived from a fluoroolefin of the formula:



wherein A and B are, the same or different, each a fluorine atom or a chlorine atom, 50 to 5 % by mole of repeating units derived from perfluorovinyl ether of the formula:



wherein Y is the same as defined above, R_1 is a C_1 - C_8 fluoroalkyl group, and p is an integer of 0 to 5 and repeating units derived from the perfluorovinyl ether (I) of the invention in an amount of 0.1 to 5 % by mole based on the total mole of the fluoroolefin (II) and the perfluorovinyl ether (III). The terpolymer according to this embodiment may further comprises at least one of other ethylenically unsaturated compounds as described above. The amount of other ethylenically unsaturated compound may be 0.1 to 20 % by mole based on the total mole of the above three compounds (I), (II) and (III).

According to the second preferred embodiment of the present invention, a copolymer comprises 20 to 90 % by mole of repeating units derived from vinylidene fluoride, 10 to 80 % by mole of repeating units derived from at least one ethylenically unsaturated compounds except vinylidene fluoride and repeating units derived from the fluorovinyl ether (I) of the invention in an amount of 0.01 to 3 % by mole based on the total mole of vinylidene fluoride and other ethylenically unsaturated compound. As other ethylenically unsaturated compound, a mixture of 10 to 45 % by mole of hexafluoropropylene and 0 to 35 % by mole of tetrafluoroethylene is preferably used.

According to the third preferred embodiment of the present invention, a copolymer comprises 20 to 100 % by mole of repeating units derived from vinylidene fluoride, 80 to 0 % by mole of repeating units derived at least one ethylenically unsaturated compounds except vinylidene fluoride and repeating units derived from the fluorovinyl ether (I) of the invention in an amount of 5 to 60 % by mole, preferably 10 to 50 % by mole based on the total mole of vinylidene fluoride and other ethylenically unsaturated compound.

According to the fourth preferred embodiment of the present invention, a copolymer comprises repeating units derived from tetrafluoroethylene and repeating units derived from the fluorovinyl ether (I) of the invention in an amount of 0.01 to 2 % by mole, preferably from 0.03 to 1 % by mole based on the mole of tetrafluoroethylene.

The elastomeric copolymer of the invention may be prepared by a per se conventional method which is employed to polymerize the conventional ethylenically unsaturated compound to produce an elastomeric copolymer. For example, the monomers are copolymerized by emulsion polymerization in the presence of a perfluoroemulsifier and a water-or oil-soluble peroxide, although they may be polymerized by bulk, suspension or solution polymerization.

In the solvent or emulsion polymerization, preferably used is a highly fluorinated solvent (e.g. dichlorodifluoromethane, trichlorofluoromethane, chlorodifluoro methane, 1,1,2-trichloro-1,2,2-trifluoroethane, 1,2-dichloro-1,1,2,2-tetrafluoroethane, 1,1,2,2-tetrachloro-1,2-difluoroethane, perfluorocyclobutane and perfluorodimethylcyclobutane).

Polymerization is usually initiated with an organic polymerization initiator. Preferred examples of the polymerization initiators are highly fluorinated peroxides, particularly a diacylperoxide of the formula:



wherein R_1' is a perfluoroalkyl group, a ω -hydroperfluoroalkyl group or a perchlorofluoroalkyl group.

The polymerization temperature depends on a decomposition temperature of the polymerization initiator and preferably from 0 to 130°C.

The polymerization pressure may be from 5 to 50 $\text{kg/cm}^2\text{G}$.

The molecular weight of the elastomeric copolymer of the invention can be easily controlled by the addition of a chain transfer agent. Specific examples of the chain transfer agent are a C_1 - C_8 hydrocarbon, an alcohol, an ether and a halogen-containing organic compound (e.g. CCl_4 , CBrCl_3 , $\text{CF}_3\text{BrCFBrCF}_3$ and CF_3I_2). When an iodine-containing fluorocarbon (e.g. CF_3I_2 , $\text{I}(\text{CF}_2)_n\text{I}$ and $\text{CF}_2=\text{CF}(\text{CF}_2)_n\text{I}$) is used as the chain transfer agent, an iodine atom is bonded at a chain end of the copolymer and still radically active. Therefore, the copolymer can be advantageously cross-linked with peroxid as a radical source in the presence of a polyfunctional unsaturated compound (e.g. triallylisocyanurate and triallylcyanurate).

In general, the elastomeric copolymer of the invention can be cured in the presence of at least one cross-linking source. A preferred example of the cross-linking source is an organic peroxide, although radioactive rays (e.g. alpha-ray, beta-ray, gamma-ray and X-ray) and a high energy electromagnetic wave (e.g. ultraviolet light) may be used as the cross-linking source.

When the organic peroxide is used as the cross-linking source, it is used in an amount of 0.05 to 10 parts by weight, preferably 1.0 to 5 parts by weight per 100 parts by weight of the copolymer.

The organic peroxide includes those easily generate a peroxy radical in the presence of heat energy or an oxidation-reduction system. Its examples are 1,1-bis(t-butylperoxy)-3,5,5-trimethylcyclohexane, 2,5-dimethylhexane-2,5-dihydroperoxide, di-t-butylperoxide, t-butylcumylperoxide, dicumylperoxide, α,α' -bis(t-butylperoxy)-p-diisopropylbenzene, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, 2,5-dimethyl-2,5-(t-butylperoxy)hexane-3, benzoylperoxide, t-butylperoxybenzene, 2,5-dimethyl-2,5-di(benzoylperoxy)-hexane, t-butylperoxymaleic acid, t-butyl peroxyisopropyl carbonate and the like. Among them, the dialkyl type peroxides are preferred. The amount and kind of the peroxide are selected according to the amount of active -O-O-groups and cross-linking conditions such as a decomposition temperature of the peroxide.

When the organic peroxide compound is used as the cross linking source, cross-linking is facilitated by the addition of a cross-linking coagent. As the cross-linking coagent, any of conventional ones may be used insofar as it is reactive with the peroxy radical and the polymer radical. Their preferred examples are triallylcyanurate, triallylisocyanurate, triacrylformal, triallyltrimeritate, N,N'-m-phenylenebismaleimide, dipropargyl terephthalate, diallyl phthalate, tetraallyl teraphthalamide, triallyl phosphate and the like. The amount of the cross-linking coagent is from 0.1 to 10 parts by weight, preferably from 0.5 to 5 parts by weight per 100 parts by weight of the copolymer to be cross-linked.

The copolymer of the invention may be blended and cocross-linked with at least one of other polymer. Examples of such cocross-linkable other polymer are silicone oil, silicone rubber, ethylene-vinyl acetate copolymer, poly-1,2-butadiene, fluorosilicone oil, fluorosilicone rubber, fulorophosphazene rubber, hexafluoropropylene-ethylene copolymer, tetrafluoroethylene-propylene copolymer and the like. Further, a polymer having radical reactivity may be blended and cocross-

linked with the copolymer of the invention. The amount of the blended polymer may be such amount that the characteristic properties of the copolymer of the invention are not deteriorated.

The elastomeric copolymer of the invention may contain a pigment for coloring the product, a filler or a reinforcing material. Usually used filler or reinforcing material includes, as an inorganic material, carbon black, titanium oxide (TiO_2), silica, clay and talc, and as an organic material, fluorine-containing polymers (e.g. polytetrafluoroethylene, polyvinylidene fluoride, polyvinyl fluoride, polychlorotrifluoroethylene, tetrafluoroethylene-ethylene copolymer and tetrafluoroethylene-vinylidene fluoride copolymer).

The curing component may be blended in the copolymer of the invention by a suitable method depending on viscoelasticity and form of the materials to be blended. The powder materials are mixed by means of open rolls or a powder mixer, while the liquid materials are mixed by means of a conventional mixer. Further, the solid materials may be dispersed or dissolved in a solvent and mixed.

The cross-linking conditions depend on the kind of the peroxide. In general, press cure is carried out at a temperature of 120 to 200°C for 5 to 30 minutes, and oven cure is carried out at a temperature of 150 to 250°C for 1 to 24 hours.

The elastomeric copolymer of the present invention can be used as a molding material, a sealant, an adhesive or a coating in various fields in which a polymeric material is required to have good chemical resistance, thermal resistance, oil resistance and/or solvent resistance.

The resinous copolymer of the invention, particularly the modified PTFE may be produced by suspension polymerization followed by finely grinding (a granular type resin) or emulsion polymerization followed by coagulation of latex (a fine powder type resin). The polymerization procedure may be the same as used for produce PTFE or conventional modified PTFE. For example, the suspension polymerization is described in Japanese Patent Publication Nos. 25398/1976 and 31524/1984, and the emulsion polymerization is described in U.S. Patent No. 2,965,595. Generally, modified PTFE of the invention is produced as follows:

In a temperature-controllable reaction vessel equipped with a stirrer, deionized deoxidized water and various additives are added and replaced with nitrogen gas several times. After the vessel is pressurized with tetrafluoroethylene, the fluorovinyl ether (I) and the polymerization initiator are added. The reaction pressure is usually kept at 4 to 30 kg/cm²G by the injection of tetrafluoroethylene. The

reaction temperature is kept from 10 to 120°C. In the suspension polymerization, the reaction mixture is vigorously stirred to disperse the produced powdery polymer, while in the emulsion polymerization, it is gently stirred to stabilize the formed latex. To improve the stability of the latex, a hydrocarbon having 12 or more carbon atoms which is inert to the polymerization reaction may be added to the emulsion polymerization system. Examples of the additives are a buffer, a molecular weight regulating agent (a chain transfer agent), a polymerization initiating aid, a non-tackifier, a fluorine-containing dispersing agent (a surfactant) and the like. The major difference between the suspension polymerization and the emulsion polymerization resides in that the former utilized a little or no dispersing agent, while the latter used the dispersing agent in such an amount as to stabilize the latex particles, for example, about 100 to 10,000 ppm.

Modified PTFE of the invention has superior properties to non-modified PTFE. For example, granular type modified PTFE of the invention can be molded by compression molding or ram injection molding and a sintered molded article has improved creep resistance. The fine powder of the modified PTFE can be molded by past extrusion and an unsintered molded article has better mechanical strength.

The copolymer of the present invention comprising the fluorovinyl ether (I) is a highly reactive polymer since it contains side chains having reactive halogen atoms (e.g. iodine, bromine and chlorine). Such the reactive halogen atoms may be converted to other functional groups such as hydrophilic groups (e.g. hydroxyl groups, carboxyl groups and sulfonic acid groups) by per se conventional methods. The copolymer having the hydrophilic groups in the side chains may be used as an ion exchange resin with good heat and chemical resistance. Further, it may be used as a separating, filtrating or sieving hydrophilic film, or a biomaterial.

The present invention will be explained further in detail by following examples, wherein parts are by weight unless otherwise indicated.

Preparation of acyl fluoride

Reference Example 1

2,2,3-Trifluoropropionyl fluoride

In a 5 liter flask equipped with a stirrer, a condenser and a dropping funnel, carbon tetrachloride (360 ml) and aluminum chloride (108 g) were charged and kept at a temperature of 30 to 35°C. Then, 2,2,3,3-tetrafluorooxetane (hereinafter referred to as "tetrafluorooxetane") (1,800 g) was dropwise added over 2 hours with stirring. To complete the reaction, three portions of aluminum chloride (each 30 g) were added every 1.5 hours. Then, the reaction was continued at a temperature of 27 to 29°C for 4 hours. The reaction mixture was distilled to give the entitled compound (1,130 g). B.P. 23-23.5°C.

Reference Example 2

2,2,5,5,6,6,7-Heptafluoro-4-oxa-heptanoyl fluoride and 2,2,5,5,6,6,9,9,10,10-decafluoro-4,8-dioxoundecanoyl fluoride

In the same flask as used in Reference Example 1, 2,2,3-trifluoropropionyl fluoride (1,059 g), crown ether (5 g), cesium fluoride (40 g) and monoglyme (1,000 ml) were charged. Then, tetrafluorooxetane (1,515 g) was dropwise added with stirring at a temperature of 15 to 20°C over 3.5 hours. Thereafter, the reaction was continued with stirring at a temperature of 15 to 20°C for 5 hours. The reaction mixture was distilled under reduced pressure to give 2,2,5,5,6,6,7-heptafluoro-4-oxa-heptanoyl fluoride (300 g. B.P. 62-64°C/80 mmHg) and 2,2,5,5,6,6,9,9,10,10-decafluoro-4,8-dioxoundecanoyl fluoride (264 g. B.P. 23°C/5 mmHg).

Reference Example 3

2,2-Difluoro-3-iodopropionyl fluoride

In a four necked 3 liter flask, dry tetraglyme (1,500 ml) was charged and then sodium iodide (825 g) was completely dissolved therein. Thereafter, tetrafluorooxetane (650 g) was dropwise added at a temperature of 30 to 40°C over 45 minutes. The reaction mixture was distilled at a temperature of 38 to 40°C under reduced pressure of 30 mmHg to give the entitled compound (1,050 g). B.P. 95-96°C.

Preparation of the fluorovinyl ether (I)

Example 1

Perfluoro(6,6-dihydro-3-oxa-1-hexene)



(a) In a four necked 3 liter flask containing cesium fluoride (88 g) and tetraglyme (34 ml), 2,2,3-trifluoropropionyl fluoride prepared in Reference Example 1 (1,055 g) was added. Then, hexafluoropropylene (hereinafter referred to as "HFPO") was injected at a temperature of -10 to -15°C at such a rate that the reaction mixture was refluxed by a dry ice cooled condenser. After 52 hours from the initiation of the reaction, the injection of HFPO was terminated and methanol (1,324 ml) was added with cooling by ice water. The reaction mixture was washed with water several times and distilled to give a compound (804 g) of the formula:



B.P. 38°C.

(b) The methyl ester (1) prepared in the previous step (a) was charged in 2 liter flask and saponified with a 10 % by weight solution of sodium hydroxide in methanol at a temperature of 60 to 70°C with using phenolphthalein as a pH indicator. From a resulting slightly pink colored viscous solution, methanol was distilled off under reduced pressure and the residue was dried under reduced pressure until a constant weight was reached to give a solid material - (810 g).

To a 3 liter flask connected with a dry ice cooled trap, the ground solid material was added and replaced with nitrogen gas. Then, the flask was heated from 150°C to 250°C in a stream of nitrogen over 5 hours. The trap contained a liquid, which was distilled to give the entitled compound. - (324 g). B.P. 61-62°C.

Example 2

Perfluoro(6,6,10,10-tetrahydro-3,7-dioxa-1-decene)



In the same manner as in Example 1 but using $\text{FCH}_2\text{CF}_2\text{CF}_2\text{OCH}_2\text{CF}_2\text{COF}$ (204 g) prepared in Reference Example 2, the reactions were carried out to give the entitled compound (65 g). B.P. 44-45°C/13 mmHg.

Example 3

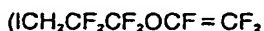
Perfluoro(6,6,10,10,14,14-hexahydro-3,7,11-trioxa-1-tetradecene)



In the same manner as in Example 1 but using $\text{FCH}_2\text{CF}_2\text{CF}_2\text{OCH}_2\text{CF}_2\text{CF}_2\text{OCH}_2\text{CF}_2\text{COF}$ (321 g) prepared in Reference Example 3, the reactions were carried out to give the entitled compound (54 g). B.P. 88-89°C/13 mmHg.

Example 4

Perfluoro(6,6-dihydro-6-iodo-3-oxa-1-hexene)



(a) In a four necked 2 liter flask, cesium fluoride (43 g), tetraglyme (6 ml) and 2,2-difluoro-3-iodo-propionyl fluoride prepared in Reference Example 4 (400 g) were charged. Then, HFPO was injected at 10°C at such a rate that the reaction mixture was refluxed by a dry ice cooled condenser. After 21 hours from the initiation of the reaction, the injection of HFPO was terminated and methanol (300 ml) was added with cooling by ice water. The reaction mixture was washed with water several times and distilled to give a compound (205 g) of the formula:



B.P. 114-115°C/100 mmHg.

(b) The methyl ester (2) prepared in the previous step (a) was charged in 1 liter flask and saponified with a 10 % by weight solution of sodium hydroxide in methanol at a temperature of 60 to 70°C with using phenolphthal in as a pH indicator. From a

resulting solution, methanol was distilled off and the residue was dried under reduced pressure until a constant weight was reached to give a slightly pinkish white solid material (202 g).

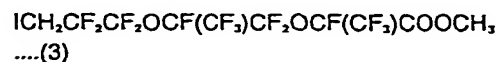
To a liter flask connected with a dry ice cooled trap, the ground solid material was added and replaced with nitrogen gas. Then, the flask was heated from 150 to 250°C under reduced pressure of 25 mmHg over 3 hours. The trap contained a purple liquid (148 g), which was distilled to give the entitled compound (81 g). B.P. 71-72°C/100 mmHg.

Example 5

Perfluoro(9,9-dihydro-9-iodo-5-trifluoromethyl-3,6-dioxa-1-nonene



(a) In a four necked 2 liter flask, cesium fluoride (60 g), tetraglyme (10 ml) and 2,2-difluoro-3-iodo-propionyl fluoride prepared in Reference Example 4 (600 g) was added. Then, HFPO was injected at 10°C at such a rate that the reaction mixture was refluxed by a dry ice cooled condenser. After 30 hours from the initiation of the reaction, the injection of HFPO was terminated and methanol (500 ml) was added with cooling by ice water. The reaction mixture was washed with water several times and distilled to give a compound (116 g) of the formula:



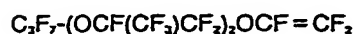
B.P. 91-92°C/6 mmHg.

(b) The methyl ester (3) prepared in the previous step (a) was thermally decomposed in the same manner as in Example 3, step - (b) to give the entitled compound (63.5 g). B.P. 87-87.5°C/45 mmHg.

Preparation of copolymers

Example 6

In a glass-lined 3 liter autoclave containing pure water 1,660 ml cooled at 5°C, a compound of the formula:



(hereinafter referred to as $\Phi_2\text{VE}$) (300 g), a compound of the formula:



(7.6 g) as a monomer for providing a cross-linking site, $\text{C}_7\text{F}_{15}\text{COONH}_4$ (15 g) and a solution of 1,3,5-trichloroperfluorohexanoyl peroxide in 1,1,2-trichloro-1,2,2-trifluoroethane (concentration, 0.44 g/ml) (9.6 ml) were charged and an interior atmosphere was quickly replaced with tetrafluoroethylene repeatedly. Then, tetrafluoroethylene was injected at 5°C to pressurize to 2.2 kg/cm²G.

As the reaction proceeded, the pressure dropped. When the pressure dropped to 2.0 kg/cm²G, tetrafluoroethylene was injected to repressurize to 2.2 kg/cm²G. With repeating decrease and increase of pressure, the polymerization was continued for 28 hours and 40 minutes.

After the polymerization was completed, the unreacted monomers were purged and then the polymerization product was recovered, washed with water and dried to give a copolymer containing 28 % by mole of $\Phi_2\text{VE}$ (182 g). Iodometry of the copolymer revealed that the copolymer contained 0.69 % by mole of $\text{ICH}_2\text{CF}_2\text{CF}_2\text{OCF}=\text{CF}_2$.

Examples 7 to 10

In the same manner as in Example 6 but using a solution of 1,3,5-trichloroperfluorohexanoyl peroxide (DLP) in 1,1,2-trichloro-1,2,2-trifluoroethane - (0.44 g/ml) and the following fluorovinyl ether of the invention in amounts shown in Table 1, the polymerization was carried out under reaction pressure for a period of time as shown in Table 1 to give a polymer:

(Examples 7 to 9)



(Example 10)



Yield and the contents of the fluorovinyl ether of the invention and $\phi_2\text{VE}$ are shown in Table 1.

Table 1

Example No.	7	8	9	10
<u>Conditions</u>				
Reaction pressure (kg/cm ² G)	1.8-2.2	1.6-2.2	1.8-2.2	1.8-2.2
Reaction time	30 hr	42 hr 10 min	41 hr	28 hr
DLP (ml)	5.3	5.3	2.6	9.6
Fluorovinyl ether (g)	4.4	2.96	4.45	11.3
<u>Results</u>				
Yield (g)	125.3	150.7	98.8	173
Content of fluorovinyl ether (mole %)	0.58	0.32	0.76	0.75
Content of $\phi_2\text{VE}$ (mole %)	---	26	---	29

To the copolymer prepared in one of Examples 6 to 10, the components as shown in Table 2 were added to prepare a curing composition and its curing properties were examined by means of a curastometer (JSR II type). The composition was

press cured at 160°C for 10 minutes and oven cured at 180°C for 4 hours and physical properties of the cured composition were measured according to JIS K 6301. The results are shown in Table 2.

45

50

55

Table 2

Example No.	6	7	8	9	10	Comp.1
Copolymer (parts)	100	100	100	100	100	100
MT-carbon (parts)	10	10	10	20	10	1
Triallylisocyanurate (parts)	4.0	4.0	4.0	3.0	4.0	4.0
Perhexa-2,5B (parts)	1.5	1.5	1.5	1.0	1.5	1.5
v_{\min} (kg)	0.03	0.01	0.01	0.04	0.03	0.04
v (kg)	3.45	1.14	1.5	2.55	3.65	No increase of torque
T_{10} (min.)	1.1	1.1	1.0	0.9	1.1	
T_{90} (min.)	5.7	3.7	3.8	2.4	5.0	
R (min.)	4.6	2.6	2.8	1.5	3.9	
M_{100} (kg/cm ²)	---	39	31	74	85	No sheet could be formed
T_B (kg/cm ²)	93	60	45	80	98	
E_B (%)	83	185	160	106	110	
Hardness (JIS, Hs)	70	65	63	83	73	

Example 11

In a 3 l reaction vessel, pure water (1 liter) and, as an emulsifier, $C_7F_{15}COONH_4$ (2 g) were charged. After replacing the interior atmosphere with nitrogen gas, $ICH_2CF_2CF_2OCF=CF_2$ (2.5 g) were injected and then, at 80°C, a mixture of vinylidene fluoride (VdF), hexafluoropropylene (HFP) and tetrafluoroethylene (TFE) in a molar ratio of 18:71:11 was injected to pressurize the interior to 16 kg/cm²G. Thereafter, a solution of ammonium persulfate (3.3 g) in pure water (80 ml) was injected together with nitrogen gas to initiate polymerization.

As the reaction proceeded, the pressure dropped. When the pressure dropped to 14 kg/cm²G, a mixture of VdF, HFP and TFE in a molar ratio of 50:30:20 was injected to repressurize to 16 kg/cm²G. With repeating decrease and increase of pressure, the polymerization was continued for 8 hours and 45 minutes with injecting $ICH_2CF_2CF_2OCF=CF_2$ (each 2.5 g) after 1.7, 3.6 and 7.1 hours from the initiation of polymerization.

After cooling the reaction vessel, the unreacted monomers were purged to give an aqueous emulsion with a solid content of 25.7 % by weight.

To the emulsion, a 5 % aqueous solution of potassium alum was added to coagulate the product. The coagulated product was washed with water and dried to give an elastomeric copolymer - (347 g). Mooney viscosity (100°C), 32. According to iodometry, the copolymer contained 0.76 % by mole of $ICH_2CF_2CF_2OCF=CF_2$.

Example 12

In a 3 l reaction vessel, pure water (1 liter) and, as an emulsifier, $C_7F_{15}COONH_4$ (2 g) were charged. After replacing the interior atmosphere with nitrogen gas, a mixture of VdF, HFP and TFE in a molar ratio of 18:71:11 was injected to pressurize the interior to 16 kg/cm²G. Thereafter, a 0.2 % by weight aqueous solution of ammonium persulfate (10 ml) was injected to initiate polymerization.

As the reaction proceeded, the pressure dropped. When the pressure dropped to 15 kg/cm²G, $I(CF_2)_I$ (1.2 g) as a chain transfer agent was injected. When the pressure further dropped to

14 kg/cm²G, a mixture of VdF, HFP and TFE in a molar ratio of 50:30:20 were injected to repressurize to 16 kg/cm²G. With repeating decrease and increase of pressure, the polymerization was continued with injecting the aqueous solution of ammonium sulfate (each 10 ml) every three hours.

When the total pressure drop reached 5 kg/cm²G (about 5 hours from the initiation of polymerization), ICH₂CF₂CF₂OCF=CF₂ (1.8 g) was injected. Further, when the total pressure drop reached 43 kg/cm²G (about 19 hours from the initiation of polymerization), the reaction vessel was cooled and the unreacted monomers were purged to give an aqueous emulsion with a solid content of 26.7 % by weight.

To the emulsion, a 5 % by weight aqueous solution of potassium alum was added to coagulate the product. The coagulated product was washed with water and dried to give an elastomeric copolymer (394 g). Mooney viscosity (100°C), 83. Intrinsic viscosity $[\eta]$, 0.53 dl/g (tetrahydrofuran, 35°C). According to iodometry, the copolymer contained 0.12 % by mole of ICH₂CF₂CF₂OCF=CF₂.

Example 13

In the same manner as in Example 12 but using 5.4 g of ICH₂CF₂CF₂OCF=CF₂ and continuing the reaction for 31 hours, the polymerization was carried out to give an elastomeric copolymer (410 g). Mooney viscosity = 48. $[\eta]$ = 0.34. Content of ICH₂CF₂CF₂OCF=CF₂ = 0.39 % by mole.

Example 14

In the same manner as in Example 12 but using 9 g of ICH₂CF₂CF₂OCF=CF₂ and continuing the reaction for 34 hours, the polymerization was carried out to give an elastomeric copolymer (398 g). Mooney viscosity = 43. $[\eta]$ = 0.31. Content of ICH₂CF₂CF₂OCF=CF₂ = 0.63 % by mole.

Example 15

In the same manner as in Example 12 but using ICH₂CF₂CF₂OCF(CF₃)CF₂OCF=CF₂ (14.9 g) in place of ICH₂CF₂CF₂OCF=CF₂ and continuing the reaction for 9.5 hours, the polymerization was carried out to give an elastomeric copolymer (383 g). Mooney viscosity = 47. Content of ICH₂CF₂CF₂OCF(CF₃)CF₂OCF=CF₂ = 0.74 % by mole.

Example 16

In the same manner as in Example 11 but using not the initial monomeric mixture, a mixture of VdF and HFP in a molar ratio of 65:35 and as the additional monomeric mixture, a mixture of VdF and HFP in a molar ratio of 78:22, using 7.2 g of ICH₂CF₂CF₂OCF=CF₂ and proceeding the reaction for 25 hours and 45 minutes, the polymerization was carried out to give an elastomeric copolymer (345 g). Mooney viscosity = 20. Content of ICH₂CF₂CF₂OCF=CF₂ = 0.52 % by mole.

Comparative Example 2

In the same manner as in Example 11 but using no ICH₂CF₂CF₂OCF=CF₂ and continuing the reaction for 5 hour, the polymerization was carried out to give a copolymer (375 g). Mooney viscosity = 87.

Comparative Example 3

In the same manner as in Example 11 but using no ICH₂CF₂CF₂OCF=CF₂ and 10 g of ammonium persulfate as a polymerization initiator and continuing the reaction for 4.1 hours, the polymerization was carried out to give a copolymer. Mooney viscosity = 43.

The vulcanizing properties of the copolymers and physical properties of the cured copolymers were measured in the same manner as in Examples 6 to 10. The results are shown in Table 3.

Table 3

Example No.	11	12	13	14	15	16	Comp.2	Comp.3
Copolymer (parts)	100	100	100	100	100	100	100	100
MT-carbon (parts)	20	20	20	20	20	20	20	20
Triallylisocyanurate (parts)	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Perhexa-2,5B (parts)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
v_{min} (kg)	0.04	0.17	0.05	0.03	0.05	0.01	0.19	0.05
v (kg)	2.98	4.45	4.80	4.70	3.05	3.87	0.30	0.21
T_{10} (min.)	0.55	0.75	0.60	0.70	0.60	0.75	---	---
T_{90} (min.)	3.30	2.05	1.90	2.80	3.00	4.70	---	---
R (min.)	2.75	1.30	1.30	2.10	2.40	3.95	---	---
M_{100} (kg/cm ²)	92	35	65	91	89	49	Foamed	
T_B (kg/cm ²)	151	198	210	204	160	168		
E_B (%)	140	290	210	180	180	190		
Hardness (JIS, Hs)	72	69	71	--	71	69		

Example 17

In a pressure resistant 100 ml glass ampoule equipped with a valve, $\text{FCH}_2\text{CF}_2\text{CF}_2\text{OCF}=\text{CF}_2$ (6.9 g), 1,1,2-trichloro-1,2,2-trifluoroethane (hereinafter referred to as "R-113") (10 ml) and a solution of 2,4,5-trichloro-perfluorohexanoylperoxide in R-113 (concentration, 0.7 g/ml (0.5 ml) were charged and cooled by dry ice-methanol followed by replacement of the interior atmosphere with nitrogen gas. Then, vinylidene fluoride (6.8 g) was added to react at a $20 \pm 1^\circ\text{C}$ for 20 minutes with shaking. As the reaction proceeded, the pressure dropped from 6.3 $\text{kg/cm}^2\text{G}$ to 5.5 $\text{kg/cm}^2\text{G}$. Thereafter, the unreacted monomers were purged, and the reaction mixture was dissolved in acetone and recovered from the ampoule. The solution was poured in pure water to precipitate the product, which was dried under reduced pressure until a constant weight was reached to give a copolymer (2.2 g).

According to $^1\text{H-NMR}$ analysis, it was found that the copolymer contained vinylidene fluoride and $\text{FCH}_2\text{CF}_2\text{CF}_2\text{OCF}=\text{CF}_2$ in a molar ratio of 71.8:28.2. Glass transition temperature (T_g) of the copolymer was measured by a differential scanning calorimeter to be -30°C . This T_g suggested that the copolymer had good low temperature properties.

Example 18

In the same glass ampoule as used in Example 17, $\text{F}(\text{CH}_2\text{CF}_2\text{CF}_2\text{O})_2\text{CF}=\text{CF}_2$ (10.8 g), R-113 (10 ml) and a solution of 2,4,5-trichloro-perfluorohexanoylperoxide in R-113 (concentration, 0.44 g/ml (0.5 ml) were charged and cooled by dry ice-methanol followed by replacement of the interior atmosphere with nitrogen gas. Then, vinylidene fluoride (5.7 g) was added to react at a $20 \pm 1^\circ\text{C}$ for 35 minutes with shaking. As the reaction proceeded, the pressure dropped from 9.8 $\text{kg/cm}^2\text{G}$ to 6.8 $\text{kg/cm}^2\text{G}$. Thereafter, the unreacted monomers were purged, and the reaction mixture was dissolved in acetone and recovered from the ampoule.

The solution was poured in pure water to precipitate the product, which was dried under reduced pressure until a constant weight was reached to give a copolymer (10.2 g).

According to $^1\text{H-NMR}$ analysis, it was found that the copolymer contained vinylidene fluoride and $\text{F}(\text{CH}_2\text{CF}_2\text{CF}_2\text{O})_2\text{CF}=\text{CF}_2$ in a molar ratio of 72.8:27.2. T_g of the copolymer was -30.5°C .

Example 19

In the same manner as in Example 17 but using $\text{F}(\text{CH}_2\text{CF}_2\text{CF}_2\text{O})_2\text{CF}=\text{CF}_2$ (14.7 g) in place of $\text{FCH}_2\text{CF}_2\text{CF}_2\text{OCF}=\text{CF}_2$ and continuing the reaction for 23 minutes, the polymerization was carried out to give a copolymer (16.2 g).

Molar ratio of vinylidene fluoride and $\text{F}(\text{CH}_2\text{CF}_2\text{CF}_2\text{O})_2\text{CF}=\text{CF}_2$ = 73.9:26.1. T_g = -42.0°C .

Example 20

In the same manner as in Example 17 but using tetrafluoroethylene (3.5 g) in place of vinylidene fluoride and continuing the reaction for one hour, the polymerization was carried out to give a copolymer (0.7 g). Any melting point was not observed since the copolymer was elastomeric. T_g = 8.5°C .

Examples 21-25

In the same manner as in Example 17 but using monomers as shown in Table 4 and continuing the reaction for a period of time shown in Table 4, polymerization was carried out to give a copolymer, a molar contents of the monomers and T_g of which are shown in Table 4.

In Table 4, "VdF", "TFE", "FM" and "DLP" represent "vinylidene fluoride", "tetrafluoroethylene", $\text{FCH}_2\text{CF}_2\text{CF}_2\text{OCF}=\text{CF}_2$ and "a solution of 2,4,5-trichloro-perfluorohexanoylperoxide in R-113 (concentration, 0.7 g/ml)", respectively.

Table 4

Example No.	21	22	23	24	25
Monomers					
VdF (g)	0.6	1.8	5.5	0.5	1.4
TFE (g)	0.2	0.7	2.2	0.5	1.4
FM (g)	6.9	6.9	6.9	6.9	6.9
Solvent					
R-113 (ml)	10	10	10	10	10
Initiator					
DLP (ml)	0.5	0.5	0.5	0.5	0.5
Temperature (°C)	20	20	20	20	20
Time (minutes)	30	20	15	30	20
Yield (g)	0.6	1.0	1.6	0.5	1.0
Monomer content					
VdF (mole %)	47.9	51.7	57.9	35.6	42.0
TFE (mole %)	3.6	9.4	15.4	27.9	25.9
FM (mole %)	48.5	38.9	26.7	36.5	32.1
T_g	-20	-33	-36.5	-44.5	-30

Example 26

In the same manner as in Example 17 but using ethylene (0.8 g) in place of vinylidene fluoride and continuing the reaction for 20 minutes, the polymerization was carried out to give a copolymer (0.8 g).

Molar ratio of ethylene and $F(CH_2CF_2CF_2O)-_nCF=CF_2 = 56.3:43.7$. $T_g = -11^\circ C$.

Example 27

In a 3 liter stainless steel autoclave equipped with a temperature controlling jacket, a stirrer and baffles, deionized deoxidized water (1.45 l) and ammonium tertiary phosphate (3 mg) were charged followed by the addition of ammonium perfluorooctanoate (9 mg). The autoclave was evacuated, injected by nitrogen gas and again evacuated. Evacuation and nitrogen injection were repeated three times. Then, injection and evacuation of tetrafluoroethylene were repeated twice. After the final evacuation, $FCH_2CF_2CF_2OCF=CF_2$ (1.2 g) was added. Thereafter, the content was heated to $70^\circ C$ with stirring at 400 rpm. Tetrafluoroethylene was injected to pressurize the interior to $7.5 \text{ kg/cm}^2 G$, and a solution of ammonium persulfate (4.0 mg) in water (50 ml) was injected together with tetrafluoroethylene to pressurize the interior to 8.0

$\text{kg/cm}^2 G$. When the pressure started to drop, tetrafluoroethylene was continuously injected to maintain the pressure at $8.0 \text{ kg/cm}^2 G$ till 250 g of tetrafluoroethylene was consumed. Then, tetrafluoroethylene was purged and stirring was stopped to terminate the polymerization.

The resultant powdery product was recovered and charged in a mixer containing water and mixed and pulverized for one minutes. The product was washed by changing water in the mixer for 5 minutes. Then, fine powder of the product was dried at $150^\circ C$ for 14 hours.

From the dried powder, a film was molded and subjected to IR spectrum analysis to find that characteristic absorption peaks at 956 cm^{-1} and $1,003 \text{ cm}^{-1}$ were present, which peaks are not found in IR spectrum of polytetrafluoroethylene.

From the ratio of the absorbances at 956 cm^{-1} and $2,360 \text{ cm}^{-1}$, the content of $FCH_2CF_2CF_2OCF=CF_2$ in the resulting copolymer was calculated based on a calibration curve. The content of $FCH_2CF_2CF_2OCF=CF_2$ was 0.1 % by mole.

Creep of the molded article of the polymer was 3.5 % at $24^\circ C$.

Creep is measured as follows:

A powdery polymer (190 g) is charged in a cylindrical metal mold having a diameter of 50 mm, compress molded under pressure of 300 kg/cm^2 for 5 minutes and removed from the mold. The mol-

ded polymeric article is sintered by heating it in a furnace up to 365°C at a heating rate of 50°C/hr, kept at the same temperature for 5 hours and then cooled to a room temperature at a rate of 50°C/hr. The sintered article is cut to form a cylindrical rod having a diameter of 11.3 mm and a height of 10 mm with coinciding the axis direction of the rod

with the compression direction. On the rod, a load of 140 kg/cm² is applied in the axis direction at a constant temperature of 24°C. Then, the height of the rod is measured after 10 seconds and 24 hours and creep (%) is calculated according to the following equation:

$$\text{Creep} = \frac{\text{Height aft. 10 sec.} - \text{Height aft. 24 hrs.}}{\text{Original height}} \times 100$$

Comparative Example 4

In the same manner as in Example 27 but using no FCH₂CF₂CF₂OCF=CF₂, the polymerization was carried out to give polytetrafluoroethylene, creep of which was 8.6 % at 24°C.

Example 28

In the same autoclave, deionized deoxidized water (1.45 l), liquid paraffin (100 ml) and ammonium perfluorooctanoate (1.5 g) were charged, and injection and evacuation of nitrogen and tetrafluoroethylene were repeated in the same manner as in Example 27. After the final evacuation, FCH₂CF₂CF₂OCF=CF₂ (1.0 g) was added. Thereafter, the content was heated to 70°C with stirring at 250 rpm. Tetrafluoroethylene was injected to pressurize the interior to 7.5 kg/cm²G, and a solution of ammonium persulfate (11.3 mg) in water (50 ml) was injected together with tetrafluoroethylene to pressurize the interior to 8.0 kg/cm²G. Tetrafluoroethylene was continuously injected at 70°C to maintain the pressure at 8.0 kg/cm²G till 730 g of tetrafluoroethylene was consumed. Then, tetrafluoroethylene was purged and stirring was stopped to terminate the polymerization.

The resultant dispersion was diluted with water and stirred together with ammonium carbonate to form a powdery product, which was dried at 130°C for 14 hours.

The content of FCH₂CF₂CF₂OCF=CF₂ in the polymer was 0.04 % by mole.

The dried powder was paste extruded under conditions as described in Japanese Patent Publication No. 28334/1984 (corresponding U.S. or European patent or application ?). The extruded article obtained in a stabilized stage was dried to

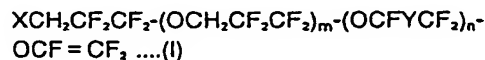
remove the extruding aid and cut to form three sample rods each having a length of about 10 cm. The sample rods were subjected to tensile test at a pulling rate of 20 cm/min., and tensile strength at break was measured and averaged for three samples. Extrusion pressure was 153 kg/cm², and tensile strength at break was 45 kg/cm².

Comparative Example 5

In the same manner as in Example 28 but using no FCH₂CF₂CF₂OCF=CF₂, the polymerization was carried out to give polytetrafluoroethylene. Extrusion pressure was 110 kg/cm², and tensile strength at break was 24 kg/cm².

Claims

1. A fluorovinyl ether of the formula:



wherein X is a hydrogen atom or a halogen atom; Y is a fluorine atom or a trifluoromethyl group; m is an integer of 0 to 5; and n is 0, 1 or 2

2. The fluorovinyl ether according to claim 1, wherein X is a halogen atom selected from the group consisting of fluorine, chlorine, bromine and iodine.

3. A copolymer comprising repeating units derived from a fluorovinyl ether (I) according to claim 1 and from at least one ethylenically unsaturated compound.

4. The copolymer according to claim 3, wherein the ethylenically unsaturated compound is one select-

ed from the group consisting of ethylene, propylene, butylene, vinyl carboxylate such as vinyl acetate, vinyl ether such as methyl vinyl ether and ethyl vinyl ether, vinyl chloride, vinylidene chloride, acrylic acid, methacrylic acid, tetrafluoroethylene, trifluoroethylene, chlorotrifluoroethylene, vinyl fluoride, vinylidene fluoride, hexafluoropropylene, pentafluoropropylene, hexafluoroisobutene, perfluorocyclobutene, perfluoro(methylcyclopropylene), perfluoroallene, α,β,β -trifluorostyrene, perfluorostyrene, perfluoroalkyl vinyl ether such as perfluoro(methyl vinyl ether) and perfluoro(propyl vinyl ether), perfluoro(alkyl vinyl polyether), polyfluoroacrylic acid, polyfluorovinyl acetate, polyfluorovinyl ether sulfonate and polyfluorodienes.

5. The copolymer according to claim 3, which comprises 50 to 95 % by mole of repeating units derived from a fluoroolefin of the formula:



wherein A and B are, the same or different, each a fluorine atom or a chlorine atom, 50 to 5 % by mole of repeating units derived from perfluorovinyl ether of the formula:



wherein Y is the same as defined above, R_f is a C_1 - C_6 fluoroalkyl group, and p is an integer of 0 to 5 and repeating units derived from the perfluorovinyl ether (I) in an amount of 0.1 to 5 % by mole based on the total mole of the fluoroolefin (II) and the perfluorovinyl ether (III).

6. The copolymer according to claim 5, which

further comprises at least one of other ethylenically unsaturated compounds in an amount of 0.1 to 20 % by mole based on the total mole of the three compounds (I), (II) and (III).

5.

7. The copolymer according to claim 3, which comprises 20 to 90 % by mole of repeating units derived from vinylidene fluoride, 10 to 80 % by mole of repeating units derived from at least one ethylenically unsaturated compounds except vinylidene fluoride and repeating units derived from the fluorovinyl ether (I) in an amount of 0.01 to 3 % by mole based on the total mole of vinylidene fluoride and other ethylenically unsaturated compound.

15

8. The copolymer according to claim 7, where in other ethylenically unsaturated compound is a mixture of 10 to 45 % by mole of hexafluoropropylene and 0 to 35 % by mole of tetrafluoroethylene.

20

9. The copolymer according to claim 3, which comprises 20 to 100 % by mole of repeating units derived from vinylidene fluoride, 80 to 0 % by mole of repeating units derived at least one ethylenically unsaturated compounds except vinylidene fluoride and repeating units derived from the fluorovinyl ether (I) of the invention in an amount of 5 to 60 % by mole based on the total mole of vinylidene fluoride and other ethylenically unsaturated compound.

30

10. The copolymer according to claim 3, which comprises repeating units derived from tetrafluoroethylene and repeating units derived from the fluorovinyl ether (I) of the invention in an amount of 0.01 to 2 % by mole based on the mole of tetrafluoroethylene.

40

45

50

55

16